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National Dioxin Study Tier 4 Combustion Sources: Project Plan

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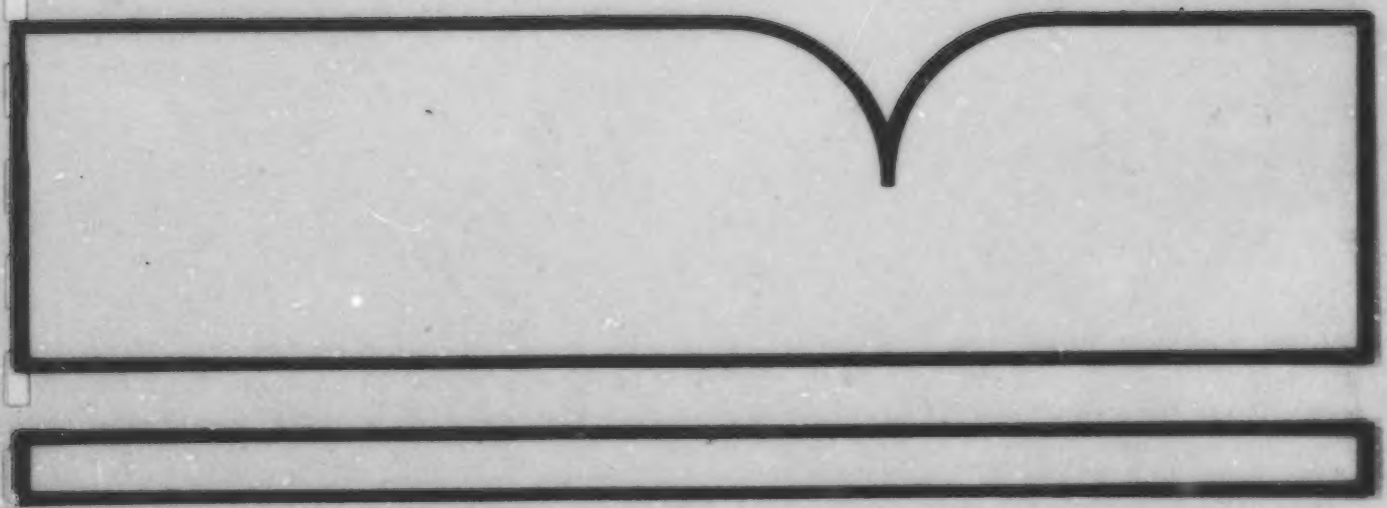

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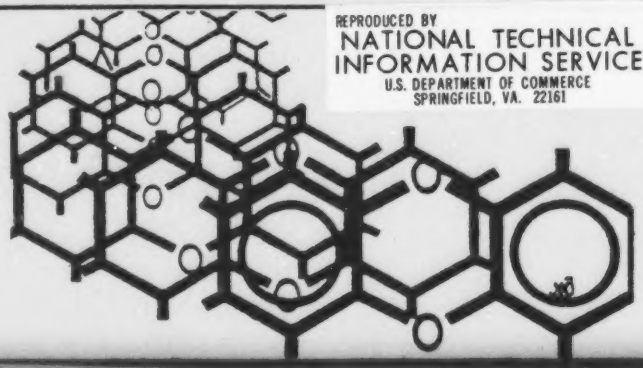
National Dioxin Study Tier 4 — Combustion Sources

Project Plan



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16. ABSTRACT

This report presents the Agency's plans for identifying likely sources and assessing dioxin emissions from combustion sources under Tier 4 of the National Dioxin Study. The primary objectives of Tier 4 are outlined in the report. These are to determine what source categories emit dioxin, at what concentrations and at what estimated exposure risk. The report describes the rationale used in developing the project plan, as well as alternative approaches that were considered.

The report describes the information the Agency plans to collect to improve the current understanding of combustion sources which emit dioxin to the ambient air. The tasks to collect the information are outlined, including stack testing, ash sampling, and data analysis. References to other documents which describe methods and procedures are identified.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Dioxins Furans 2378 Tetrachlorodibenzo-p-dioxin TCDD TCDF PCDD PCDF National Dioxin Study Air Toxic Studies Combustion Sources NDS Tier 4 Waste Combustion Wood Stoves Mobile Sources	Air Pollution Studies	

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Project Plan

By
Air Management Technology Branch

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, NC 27711

February 1985

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Section 1

Introduction And Summary Of Tier 4 Project Plan

1.1 Introduction

This report presents the U. S. Environmental Protection Agency's (EPA's) plans for identifying likely sources and assessing the magnitude of dioxin* emissions from combustion sources under Tier 4 of the National Dioxin Study.[1] The report describes the information EPA plans to collect to improve the Agency's current understanding of combustion sources which may emit dioxin to the ambient air. This report also describes the rationale used in developing the project plan, as well as alternative approaches that were considered. While source sampling and analytical methods that will be used during the study are mentioned, this report is not intended to describe these methods in detail. References to other documents which describe methods and procedures more fully are identified.

1.2 Background

There are 75 different chlorinated dioxin isomers, divided into eight homologues, each with different physical and chemical properties.[2] One of the 22 isomers with four chlorine atoms is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD).* There are three reasons why this isomer is the principal focus of the National Dioxin Strategy:

1. It is believed to be the most toxic of the chlorinated dioxins,
2. It is the isomer most often associated with exposure and potential health risks to humans, and

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*Throughout this project plan, the terms dioxin and dioxins are used generically to indicate chlorinated dioxin compounds as distinguished from 2378-TCDD, the specific isomer of major concern.

3. There is sufficient associated health and exposure information available to allow a targeted study to be developed.

On December 15, 1983, EPA released a Dioxin Strategy[1] which provides a framework under which EPA will:

1. Study the nature and extent of contamination of 2378-TCDD and the associated risks to humans and the environment;
2. Implement or compel necessary cleanup actions at contaminated sites; and
3. Further evaluate regulatory alternatives to prevent future contamination, as well as disposal alternatives to alleviate current problems.

To implement the strategy, EPA has formed seven study tiers, ordered by the decreasing potential for 2378-TCDD contamination:

Tier 1 - 2,4,5-trichlorophenol* (245-TCP) production sites and associated waste disposal sites;

Tier 2 - Sites (and associated waste disposal sites) where 245-TCP was used as a precursor to make pesticidal products;

Tier 3 - Sites (and associated waste disposal sites) where 245-TCP and its derivatives were formulated into pesticidal products;

Tier 4 - Combustion sources;

Tier 5 - Sites where pesticides derived from 245-TCP have been and are being used on a commercial basis;

Tier 6 - Certain organic chemical and pesticide manufacturing facilities where improper quality control on certain production

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*2378-TCDD is a known contamination of 2,4,5 trichlorophenol, hence the focus on sites producing and/or handling 245-TCP.

processes could have resulted in the formation of a 2378-TCDD contaminated product waste stream; and

Tier 7 - Control sites where contamination from 2378-TCDD is not suspected.

1.3 Management Of The National Dioxin Strategy

Overall responsibility for the management of the Strategy has been assigned to the Assistant Administrator for the Office of Solid Waste and Emergency Response (OSWER). OSWER is also managing the investigations for sites in Tier 1 and 2 of the study. The Office of Water Regulations and Standards (OWRS) is managing Tiers 3, 5, 6 and 7, while the Office of Air and Radiation (OAR) is responsible for Tier 4. The Office of Research and Development (ORD) is responsible for sampling and analytical guidance. ORD is also providing analytical support for Tiers 3-7 through EPA laboratories, collectively known as the Troika.* As described later, EPA's Regional Offices are responsible for implementing various aspects of the National Dioxin Strategy, including portions of Tier 4.

1.4 Project Approach

There are many data gaps in the available information concerning emissions of dioxins from combustion sources.[3] As such, a number of different study approaches could be taken to fill these data gaps. After considering various alternatives, the Agency has decided to focus the Tier 4 effort on the collection of samples from a number of combustion source categories which are believed to have the greatest potential to emit 2378-TCDD to the ambient air. The primary objective of the Tier 4 project thus, is one of problem definition, i.e., what

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*Environmental Research Laboratory (ERL), Duluth, MN; Environmental Monitoring and Support Laboratory (EMSL), Research Triangle Park, NC; and the Office of Pesticides and Toxic Substances, Environmental Chemistry Laboratory (ECL), Bay St. Louis, MS.

source categories emit dioxin and at what concentrations? Extensive stack and ash samples from selected source categories will be collected and analyzed for 2378-TCDD and the higher dioxin and furan homologues (i.e., tetra, penta, hexa, hepta, and octa). Such efforts are needed to broaden our understanding of what combustion source categories emit dioxins and furans to the ambient air.

This approach is believed necessary for a number of reasons. Only a limited number of combustion source categories have previously been tested to determine if they emit dioxins (including 2378-TCDD) to the ambient air. While dioxin and furan compounds have been found in stack emissions and fly ash from some source categories, they have not been detected at all of the source categories which have been tested. Ranges of dioxin concentrations have been shown to be very broad (orders of magnitudes). Some of the variation in the ranges may be due, to differences in process operations within a source category [e. g., mass burn versus refuse derived fuel (RDF) as subcategories of municipal incinerators; dry process versus wet process as subcategories of RDF, etc.] but data are generally insufficient to allow such conclusions to be drawn. Also measurement methods have varied considerably within the data base now available. These and other factors, not surprisingly, have led to conflicting theories on how and when dioxins are formed. In summary, currently available data do not clearly define the magnitude and scope of dioxin (and furan) air emissions from combustion sources.[3]

The scope of the Tier 4 study must be limited, for several practical reasons. While the Tier 4 budget of over $1.3 million is a considerable sum, it does not provide the funds for the Agency to implement a comprehensive study program that can examine all aspects of dioxin emissions from combustion sources. For example, Tier 4 will not adequately answer the question of how to minimize dioxin emissions. An important factor which limits the scope of Tier 4 is the

high cost of stack sampling which is estimated to cost approximately $90,000* for each source tested. This cost does not include similarly expensive analytical work. Because of these high costs and the limited resources available, the scope of the study must be sharply focused.

Also of considerable impact is the fact that the National Dioxin Strategy is a two year effort scheduled to end in December 1985.[1] At that time, a report to Congress is planned which will summarize the results of the study. This schedule limits to some degree the types of activities which can be initiated and completed by that date. Certain research studies, such as developing and validating a mechanistic model of dioxin formation in combustion sources, which would likely take years to design and complete, would not be practical for this study.

Because all aspects of the dioxin issue cannot be included in Tier 4, followup studies may be needed. The results of the Tier 4 study should provide a reasonable basis on which to determine any need for additional studies.

1.5 Basis For Investigation Of Combustion Sources

There are several unproven hypotheses concerning dioxin emissions from combustion processes. Dow Chemical's "Chemistries of Fire" theory proposes that dioxins are a natural byproduct of fire and will be formed at some quantities in all combustion processes.[5] However, experimental results by Buser and Rappe and an evaluation of data from the literature[3] suggest that dioxins are emitted only under limited conditions. The most prevalent theories, including Esposito's formation mechanism,[2] involve the incomplete combustion of polychlorinated dibenzo dioxin (PCDD's) or PCDD precursors. Neither the Dow hypothesis nor the precursor hypothesis have been conclusively supported or refuted.[3,5] Recent

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*$90,000 is an estimate based on a typical source test, and does not include any laboratory analysis for dioxins, homologues or isomers. Actual costs will vary depending on source configuration, specific analytical work done., etc. Each work plan for individual sites will have individual estimates and costs will be optimized. See Reference 4.

studies involving pyrolysis of wood with and without chlorination, in conjunction with the studies of pyrolysis of chlorinated coal, suggest that inorganic chlorine at high levels with any organic material may very well lead to PCDD formation.

Although there is some disagreement, PCDD precursors are defined for the purpose of this plan as chlorinated aromatics that can produce PCDD's through bimolecular reactions and thermal rearrangements during incomplete combustion. Examples include chlorinated phenols and chlorinated benzenes. When PCDD's are formed in a combustion source, or are already present in fuel, they can escape in the exhaust gas stream with the fine particulate especially when the thermal destruction efficiency of the combustion process is low.[3]

The Agency has recently performed a qualitative analysis of available data considering precursors and combustion conditions believed to contribute to dioxin emissions.[3] Combustion source categories determined to have the greatest potential to emit 2378-TCDD are listed in Table 1-1. Source categories rated as "Rank A Sources" are those for which limited data are available and are believed to have the greatest potential to emit dioxin. Rank A sources will receive the highest priority for testing. Some B and C ranked Source categories will also be tested.

Since combustion sources are ubiquitous and are fairly concentrated in urban areas, it is conceivable that a large portion of the United States population may be exposed to dioxins including 2378-TCDD in the ambient air. More data are needed to determine the magnitude and extent of exposure to dioxins from combustion sources. While current evidence does not suggest that an unreasonable risk exists, the Dioxin Study provides an opportunity to perform a more orderly and thorough investigation of the issue. For each stack test by Tier 4 where dioxins are determined to be emitted to the air, the risks of dioxin emissions will be estimated.

Table 1-1. Ranked Source Category List For Stack Testing[1]

Rank A Source Categories:[2]

Sewage Sludge Incinerators
Black Liquor Recovery Boilers

Rank B Source Categories:[3]

Industrial Incinerators (including hospital incinerators)
Boilers (Firing PCP treated Wood)[4]
PCP Sludge Incinerators[4]
Carbon Regeneration (industrial)
Metal Reclamation

Rank C Source Categories:[5]

Wood Stoves
Charcoal Manufacturing
Mobile Sources
Small Spreader-Stoker Coal Boilers
Chlorinated Hazardous Waste Incinerators
Lime/Cement/Aggregate Kilns Co-fired with Chlorinated Organic Wastes
Commercial Boilers Firing Fuels Contaminated with Chlorinated Organic Wastes
Open Burning
Apartment House Flue Fed Incinerators

Rank D Source Categories:[6]

Municipal Solid Waste (MSW) Incineration
Industrial Boilers Co-firing Wastes

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[1]The list of combustion source categories under investigation by Tier 4 continues to be revised as new information is received and is therefore subject to change.

[2]Rank A are large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination of feed/fuel. These categories are judged to have a high potential to emit TCDD.

[3]Rank B are small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have some potential to emit TCDD.

[4]PCP is an abbreviation for pentachlorophenols.

[5]Rank C are source categories less likely to emit TCDD.

[6]Rank D are source categories which have already been tested three or more times.

1.6 Summary Of Tier 4 Program Plan

Two levels of source sampling are planned in Tier 4. On one level, relatively inexpensive ash samples (screening) will be collected from combustion source categories listed in Table 1-2. As explained later, these source categories are believed to have a likelihood of emitting dioxins. Ash samples will be collected from approximately three different sources in each source category. These ash samples will generally be collected from control devices, or at some other point in the device duct work downstream from the combustion zone. "Bottom" ash samples will only be taken where downstream samples are not possible. These samples will be analyzed to determine the concentration of 2378-TCDD and the higher dioxin and furan homologues present in the ash. These data will be used to provide a qualitative indication of the presence of dioxins in the flue gas emissions. Due to the uncertainties demonstrated in previous ash and stack sample comparisons, ash samples can neither be used with certainty to quantify dioxin and furan air emissions nor to conclude their absence from stack emissions.[3] However, dioxins measured in ash will identify those source categories which probably should be further tested. Tier 4 ash data will also add to the available information on the ash and stack gas relationships of dioxin.

In addition to the ash sampling program, a number of combustion source categories have been selected for detailed source testing. Because of the cost involved with stack testing, only 10 - 12 different sources can be tested from the source categories listed in Table 1-2. These stack tests will be performed using EPA's modified Method 5 and source testing procedures consistent with those described in the recently developed American Society of Mechanical Engineers (ASME) sampling protocol for waste-to-energy facilities.[6]

The samples to be collected during the stack testing program are discussed in Section 3 and are briefly summarized here. They include total stack emission samples before and after controls, ash or slurry samples from the control device

TABLE 1-2. COMBUSTION SOURCE CATEGORIES WHERE ASH SAMPLES AND STACK SAMPLES WILL BE COLLECTED[1]

Source Categories	Samples To Be Collected	
	Ash	Stack
Sewage Sludge Incinerators	X	X
Black Liquor Recovery Boilers	X	X
Industrial Incinerators (including hospital incinerators)	X	X
Metals Reclamation (including wire reclamation incinerators and secondary copper smelters)	X	X
Chemical Sludge Incinerators	X	X
Industrial Carbon Regeneration Units	X	X
Charcoal Manufacturing Ovens	X	-
Wood Stoves	X	X[2]
PCP Treated And Salt Laden Wood Combustion In Boilers	X	X
Small Spreader-Stoker Coal Fired Boilers	X	X
Kilns And Commercial Boilers Burning Hazardous Wastes	X	-
Open Burning (including forest fires and agricultural burning)	X	-
Apartment House Flue Fed Incinerators	X	-
Mobile Sources	X[2]	-

[1]The list of Tier 4 categories continues to be revised as new information is received and is therefore subject to change.
[2]Includes some samples and results being supplied to Tier 4 by other programs.

and firebox, samples of the feed or fuel, and samples of nearby soils. Precombustion air samples will also be collected at those sources where precursors are suspected to be present in significant concentration in the air from other nearby sources. A summary of the samples to be collected during stack testing and the analyses to be performed under Tier 4 are outlined in Table 1-3. Although not noted in the table, an additional number of samples will be collected and analyzed for quality assurance/quality control purposes.

Stack, ash, feed, fuel, soil and precombustion air samples for Tier 4 will be analyzed for the 2378-TCDD isomer, and for each of the higher homologues of dioxin and furans (i.e., tetra, penta, hexa, hepta, and octa). Precombustion air and feed samples will also be analyzed for selected suspect dioxin precursors (e.g., chlorophenols and chlorobenzenes). Stack samples will be collected primarily by EPA contractors who will ship them to the designated Troika laboratory for analysis. Procedures for the collection and shipping of samples, as well as the analytical and quality control procedures to be followed, are discussed elsewhere.[7]

At the conclusion of the Tier 4 study, the Agency will have collected either qualitative screening samples or detailed stack samples from a number of combustion source categories. These data should provide a better understanding of the source categories which emit dioxins and furans to the atmosphere. The detailed stack test data will allow the Agency to determine the magnitude of the dioxin and furan emissions from these sources and calculate the risk to which the people in the vicinity of such sources are exposed. Figure 1-1 presents the anticipated schedule for the Tier 4 project.

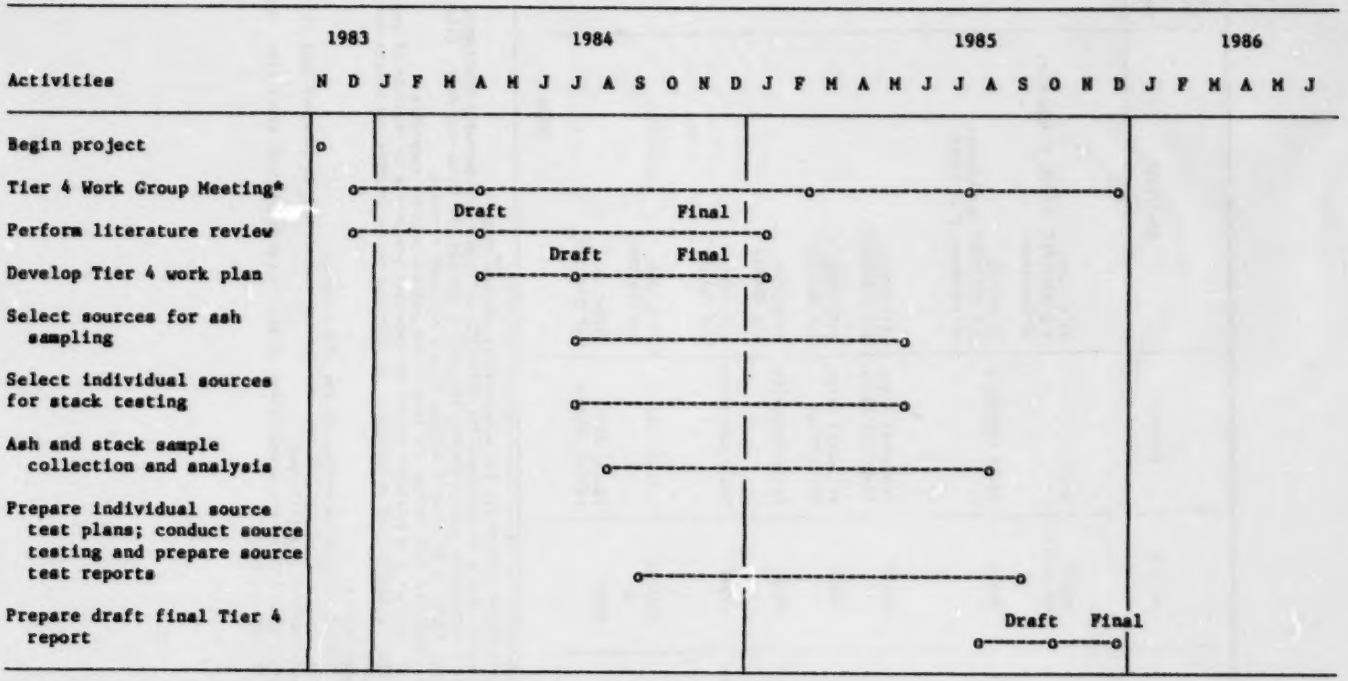
The information collected during the study will be summarized in a final report. The report will also summarize the available data from other studies. For example, stack test data being collected from various muncipal incinerators by New York State and others will be included, if available. Any preliminary

TABLE 1-3. SAMPLING AND ANALYSES MODEL

Sample	Method	Samples	Analyses[a]	Total Samples[b] for Analysis	Analysis[c] Priority
Inputs					
Precombustion Air	XAD-2 (Ambient)[d]	0-1[e]	2378-TCDD, 4-8 CDD/CDF[f], TOCL$, Cl-phenols, Cl-benzenes	1[c]	2
Waste Feed and/or Fuels	Grabs	Daily Composite	2378-TCDD, 4-8 CDD/CDF[f] Cl-phenols, Cl-benzenes, PCB, TOCL$	3[f]	2
Outputs					
Stack Before Control	MM5T[h]	Condenser Rinse Adsorbent Resin	2378-TCDD, 4-8 CDD/CDF[f]	3	2
Stack After Control	MM5T[h]	Filter(s) Catch Probe Rinse	2378-TCDD, 4-8 CDD/CDF[f]	3	1
Bottom Ash	Grabs	Daily Composite	2378-TCDD, 4-8 CDD/CDF[f]	3	1
Ash From Control Device	Grabs	Daily Composite	2378-TCDD, 4-8 CDD/CDF[f]	3	1
Other					
Soils (in vicinity)	Borings	1 Composite	2378-TCDD, 4-8 CDD/CDF[f]	1	3
Sampling Train Blanks	MM5T[h]	Resin, Filter(s), Rinses	2378-TCDD, 4-8 CDD/CDF[f]	2	1/2[i]
			TOTAL	19[j]	

[a] Precursor analysis by contractor and dioxin/furan analyses by Troika.
[b] Based on 3 sampling days. Numbers shown are for dioxin/furan samples only.
[c] Priority 1 indicates analyses should be performed for 2378-TCDD and higher (tetra-octa) homologues of dioxins and furans. If there is a detectable concentration, Priority 2 samples are to be analyzed. Priority 3 samples may be analyzed on a case-by-case basis if Priority 2 samples have a positive response.
[d] XAD-2 (ambient) denotes a modified high volume air sampler for ambient organic compounds.
[e] Sample to be collected if there is a significant source of suspected precursors in vicinity of sampling site.
[f] 4-8 CDD/CDF = Analyses done on higher (tetra through octa) chlorine number dioxins and furans with results reported as totals for each group only.
$TOCL = Total organic chlorine.
[h] MM5T is a modified EPA "Method 5" train as defined in the ASME protocol.
[i] For blank sampling trains, one is designated priority one and the second will be analyzed only if the first blank train has detectable background levels of dioxin/furans.
[j] Multiple analyses for each sample will have a multiplier effect on the analytical costs also. Total does not include quality assurance samples (approx. 20%).

FIGURE 1-1. SCHEDULE: NATIONAL DIOXIN STUDY - TIER 4 - COMBUSTION SOURCES


1983
1984
1985
1986
Activities
N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J
Begin project
Tier 4 Work Group Meeting*
Perform literature review
Draft
Final
Develop Tier 4 work plan
Draft
Final
Select sources for ash sampling
Select individual sources for stack testing
Ash and stack sample collection and analysis
Prepare individual source test plans; conduct source testing and prepare source test reports
Prepare draft final Tier 4 report
Draft
Final

*Tier 4 Work Group will meet periodically throughout the study period.

results from the three million dollar, three year effort being initiated by Environment Canada to examine the significance of various operating conditions on dioxin emissions from municipal incinerators will also be included. The Tier 4 report will also include a list of recommendations for future testing and study.

1.7 Possible Results Of The Tier 4 Study

The primary objective of this study is problem definition. The degree to which Tier 4 can satisfy this objective depends in large measure on the magnitude and pervasiveness of dioxin and furan emissions found during the study. For example, stack test data and subsequent risk assessments may indicate, at least for the sources or source categories tested, that dioxin and furan emissions are not likely to result in an unreasonable risk to the public. Assuming this is the result, some general conclusions about the scope of dioxin and furan emissions from combustion sources can be drawn. Such conclusions will obviously need to be stated carefully, acknowledging the possiblity that some untested sources may exist which may emit elevated levels of 2378-TCDD or other dioxins and furans.

A more likely outcome of the study is that the ash sampling program will identify a number of source categories with a sufficient probability of having levels of dioxins and/or furans present in the ash which merit more detailed testing. Similarly, the stack test program which can be conducted under Tier 4 may identify relatively high emission rates from some of the sources which are tested, thereby indicating a need for additional testing at similar sources. As a result, some followup studies would be needed to define more fully the magnitude of the problem.

1.8 Format Of This Report

This section has provided an overview of the scope and purpose of the Tier 4 program. Section 2 discusses various alternatives which were considered. Section 3 provides further detail on how the source categories to be tested under Tier 4 were identified, the number and types of samples to be collected and the analyses to be performed. Section 4 describes the implementation aspects, of the program, such as how individual sources were selected for testing and how the various samples will be collected.

Section 2

Alternative Study Plans Which Were Considered

The previous section presented a brief overview of the scope and purpose of the Tier 4 study. In designing the study, the Agency considered various alternatives. The most recommended alternatives are described below, along with the reasons why they were not included in the Tier 4 plan.

2.1 Alternative 1: Focus The Tier 4 Effort Primarily on Municipal Waste Incinerators

The most frequently suggested alternative was to focus the Tier 4 study, in whole or in part, on determining the magnitude of dioxin and furan emissions from various municipal waste incinerators. There were several reasons for this.

First, of the combustion source categories which have been tested, dioxin emissions are greater for this source category than for any others. This source category is, therefore, viewed with continued interest and concern. Second, a number of urban areas are presently considering the permitting of new municipal incinerators, primarily as resource recovery units, due to the limitations associated with land disposal. Solid waste program representatives and other government officials, representatives of industry, and the public are concerned about the potential exposure and risk from dioxin and furan emissions from these proposed facilities. As a result, it has been recommended that a number of municipal waste incinerators be tested in order to gain a better understanding of their dioxin and furan emissions.

After careful consideration, the Agency decided to focus the Tier 4 stack test program primarily on combustion source categories other than municipal waste incinerators for the following reasons:

(1) Six of the approximately 40 large conventional (non-modular) municipal waste incinerators in the United States have already been tested.[3] As such, this source category is by far the most tested of all combustion source categories.

(2) Based on the results of previous tests, the Agency has tentatively concluded that the emissions from well operated facilities do not pose a significant public health problem to those persons living in the vicinity of these sources. This position was initially contained in a report entitled "Interim Evaluation Of Health Risks Associated With Emissions Of Tetrachlorinated Dioxin From Municipal Waste Resource Recovery Facilities,"[8] and was reaffirmed by the Agency in December 1983.[9]

(3) It is possible that other source categories may emit similar or larger quantities of dioxins and furans or have a greater exposure and risk associated with them than municipal waste incinerators. This cannot be determined unless resources are devoted to testing other source categories, and

(4) There appears to be considerable interest in testing specific municipal waste incinerators, so that a number of municipal incinerators will be tested, even if they are not tested under Tier 4. At present, approximately ten municipal waste incinerators have tests planned or are being tested, primarily by Region III, NASA, individual States, and Environment Canada.

For these reasons, the Agency has decided not to focus the Tier 4 stack testing effort on municipal incinerators. However, available data from tests of municipal incinerators by other agencies will be obtained and included in the final Tier 4 report.

2.2 Alternative 2: Investigate Conditions Which Increase/Decrease Dioxin And Furan Emissions

Another alternative considered was to include a field study designed to examine the significance of various combustion device operating parameters on the magnitude of dioxin emissions. Under this option, detailed stack sampling would be performed at one or two facilities. Various operating conditions (such as waste load and excess air) would be carefully monitored over a range of conditions and emissions measured for correlation.

It is recognized that such work is useful and necessary to understand how dioxin emissions can be minimized. However, such a study has not been included in Tier 4. The primary reasons are the high cost to conduct such a field study and that similar studies are planned by others.

For example, Environment Canada, has recently initiated a three year, $3 million study designed to investigate the significance of changes of various operating conditions upon emissions at three municipal waste incinerators. Also, the ASME plans a similar series of tests at a United States incinerator. For these reasons, a program to collect additional field data to characterize the significance of operating parameters has not been included. However, the results of the studies previously mentioned will be obtained and summarized in the final Tier 4 report.

2.3 Alternative 3: Develop A Mechanistic Model To Estimate Dioxin And Furan Emissions

Since resources to conduct detailed stack tests for each combustion source category are not possible, it has been suggested that an empirical or mechanistic model be developed which could be used to estimate emissions of dioxins and furans from source categories which could not be stack tested. This alternative was not included in the final Tier 4 plan for the following reasons:

(1) A mechanistic or empirical model data may require a substantial amount of time to develop and validate. Given the current schedule of the National Dioxin Strategy, there is probably not sufficient time to (a) design such a model, (b) collect the necessary source test data, (c) validate the model, and (d) estimate dioxin emissions for many source categories.

(2) It is not entirely clear, if a single model could be developed which would be applicable to all combustion source categories, or whether a number of models would need to be developed for various types or groups of combustion source categories. Certain theoretical models now exist, but the practical field application of these models is believed limited at this time.

(3) The development and validation of such models may not be possible or successful, given the limited amount of test data which can be collected under Tier 4.

For these reasons, the Agency has decided not to include the development of mechanistic or empirical models as part of the Tier 4 program. However, it is anticipated that a followup project to further examine the feasibility of developing a practical empirical or mechanistic model(s) will likely be initiated at a later date. Such efforts could use the data collected under Tier 4 and other ongoing projects as a framework to design such a model development and validation program.

2.4 Alternative 4: Collect Ash Samples From A Large Number Of Source Categories

In order to determine which source categories emit dioxins and furans, it has been suggested that ash samples be collected from a large number of combustion source categories. Under this alternative, ash sampling would the primary activity of Tier 4.

A comprehensive ash sampling program in lieu of stack testing has not been included primarily because ash samples have a limited value in identifying sources which may emit dioxins.[3] A review of available data suggests that concentrations of dioxins measured in ash do not correlate sufficiently with dioxin flue gas concentrations for ash data to be used to estimate stack emissions. Although the data available tend to suggest a trend, ash sampling has limited value, even to identify which source categories emit dioxins.

Ash samples collected for Tier 4 stack sampling program will be examined for any correlation of ash data with stack emissions. It is hoped that with these additional data and studies by others, more definite statements can be made regarding the value of ash samping data.

Section 3

The Tier 4 Project Plan

3.1 Overview

This section describes the process which was used to identify those combustion source categories which are likely to have the greatest potential to emit dioxin to the ambient air. These source categories are candidates for source sampling under Tier 4. The process initially involved a literature review of information related to dioxin emissions from combustion sources.[3] The information was reviewed to determine (a) which combustion source categories had already been tested for dioxin and (b) which factors appear to be most important with respect to dioxin being emitted from combustion sources. Criteria were then applied to prioritize those source categories believed to have the greatest potential to emit dioxin.

3.2 Literature Review And Evaluation

An initial literature search for dioxin emission information was made in 1983 for OAR/EPA.[10] This literature search was used as the starting point for a more specific review of previous studies concerning dioxin emissions from combustion sources. Contacts were made to identify recently performed or on-going studies which could be used to supplement the data base. While the full results of the literature review are reported elsewhere, the following paragraphs provide a summary of the key findings of the search.[3]

3.3 Summary Of Available Data

A review of the literature[3] has identified 12 combustion source categories which have been tested for dioxins and for which data are available. Table 3-1 lists these source categories and the concentrations which have been measured.

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TABLE 3-1. COMBUSTION SOURCES FOR WHICH TCDD TEST DATA ARE AVAILABLE

Source Category	Number Of Facilities Tested	Sample	TCDD[a] Mean	TCDD[a] Range	2378-TCDD[a] Mean	2378-TCDD[a] Range	References
Municipal Waste Combustors							
o USA	6	Stack	3.5 ng/m^3	ND-240 ng/m^3	3.5 ng/m^3	0.30 - 9.1 ng/m^3	11 - 15
o European	13	Stack	25.6 ng/m^3	ND-128 ng/m^3	-[b]	-	16 - 20
Hazardous Waste Incinerators							
o Incinerator Ship	2	Stack	ND[c]	ND	-	-	21, 22
o Land Based Incinerators	10(7)[d]	Stack	0.56 ng/m^3	ND-2.5 ng/m^3	ND	*[e]	23 - 26
Sewage Sludge Incinerators	1	Stack	f	f	-	-	27
Utility Coal Boilers	7	Stack	ND	ND	-	-	12, 13
Commercial Boilers (Waste Fired)	6(6)[d]	Stack	g	g	-	-	28
Industrial Boilers (Waste Fired)	6(1)[d]	Stack	10.13 ng/m^3	ND-40.5 ng/m^3	18,000 ppt[h]	ND-55,000 ppt	5, 29 - 31
Activated Carbon Regeneration	1	Stack	0.175 ng/m^3	0.06-0.30 ng/m^3	0.10 ng/m^3	0.01 - 0.21 ng/m^3	32
Residential Combustion[i]	4	Scrapings	329 ppt	ND-777 ppt	242 ppt	26-600 ppt	5, 33
Mobile Sources[j]	9(4)[d]	Exhaust	4.0 ppt	ND-20 ppt	3.0 ppt	*	5, 34
Wire Reclamation Incinerators	1	Scrapings	234 ppt	58-410 ppt	-	-	35
Lime/Cement Kilns (Waste Fired)	1(1)[d]	Stack	g	g	-	-	36
Accidental Electrical Equipment Fires[k]	2	Wall Swipes	44 ppm[l]	ND-195 ppm	0.059 ppm	*	37, 38

[a]TCDD = Tetrachlorodibenzo-p-dioxin.
[b]Dash = No data.
[c]ND = None detected (detection limits vary).
[d]Number of tests which have been performed, but for which the results have not been officially reported.
[e]* = One datum, no range available.
[f]PCDD scan only. PCDD concentrations ranged from 483 ng/m^3 to 1,140 ng/m^3 with a mean of 739 ng/m^3.
[g]Results have not yet been officially reported.
[h]ppt = Parts per trillion by weight.
[i]Fuels include wood, wood/oil mixture, and natural gas.
[j]Fuels include diesel, unleaded and leaded gasoline. In one test series exhaust scrapings were analyzed, in the other series, filter medium from exhaust samples.
[k]Includes PCB transformers and capacitor batteries.
[l]ppm = Parts per million by weight.

General operating characteristics of the sources which were tested are summarized in Table 3-2 and are used below to identify combustion related parameters which may affect the likely presence and magnitude of dioxin emissions from combustion sources.

Dow Chemical's "Chemistries of Fire" hypothesis proposes that polychlorinated dibenzo dioxins (PCDD's) are a common and natural byproduct of fire.[5] However, an evaluation of data from the literature suggests that PCDD's are emitted during the incomplete combustion of either (a) dioxins or (b) dioxin precursors. Although uncertainty remains, dioxin precursors are defined for purposes of this project plan as chlorinated aromatics which can produce dioxins through bimolecular reactions and thermal rearrangements. Examples include chlorinated phenols and chlorinated benzenes. Based on the literature review,[3] the following factors appear to affect dioxin emissions:

- °PCDD in feed,
- °Precursors in feed,
- °Chlorine in feed,
- °Combustion temperature,
- °Residence time,
- °Oxygen availability,
- °Feed processing,
- °Supplemental fuel.

3.3.1 PCDD In Feed[3]

2378-TCDD is a "side reaction" impurity that can result from the manufacture of trichlorophenol, which is used to make the herbicide 2,4,5-trichlorophenoxy acetic acid (245-T). Pentachlorophenol (PCP) production can also result in a PCDD contaminant, primarily octachlorodibenzo-p-dioxin (OCDD). The primary end use for PCP is as a wood preservative. It is anticipated that some dioxin

TABLE 3-2. CHARACTERISTICS OF SOURCES TESTED FOR DIOXINS

Source	Precursors	Furnace Type	Temperature	Available Air[a]
Municipal Waste Combustors				
*Conventional	Cl-aromatics	Waterwall	500-1000°C	Low
*Refuse Derived Fuel Boilers	Cl-aromatics	Spreader-Stoker	1000°C	Excess
Hazardous Waste Incinerators				
*Land Based	PCBs, PCPs	Rotary Kiln	1200°C	Excess
*Incinerator Ships	PCBs, PCPs	Dual Chamber	1600°C	Excess
Sewage Sludge Incinerators	PCBs, Cl-aromatics	Multiple Hearth	450-950°C	Low
Utility Coal Boilers	Coal, Low Chlorine	Pulverized Coal	1200°C	Excess
Commercial Boilers (waste fired)	TCP	Small Fire Tube	1000°C	Excess
Industrial Boilers (waste fired)	PCP, Cl-aromatics	Liquid Injection/Stoker	1300°C	Excess
Activated Carbon Regeneration	PCBs	Fluidized Bed	750-1000°C	Limited
Residential Wood Combustion	Low Chlorine	Wood Stove/Fireplace	<500°C	Low
Mobile Sources	Low Chlorine	Internal Combustion Engine	1800-2500°C	Excess
Wire Reclamation Incinerators	PCBs, PVCs	Batch/Conveyor	500°C	Limited
Lime/Cement Kilns (waste fired)	Cl-organics	Rotary Kiln	1400°C	Excess
Accidental Transformer Fire	PCBs, Cl-benzenes	Uncontrolled PCB Oil Fire	NA[b]	NA

[a]Excess: High air/fuel ratio with efficient mixing.
Low: High air/fuel ratio with inefficient mixing.
Limited: Designed for low air/fuel ratio.
[b]NA: Not Available

contamination may also occur during the manufacturing of other similar chlorinated aromatics, particularly if the manufacturing efficiency is less than optimal. Therefore, dioxins are thought to enter the environment as a contaminant of some commerical products, such as wood preservatives and pesticides.

The widespread use of these products increases the possibility of finding dioxins in the feed of a combustion process. For example, PCP treated wood may be used to fire industrial boilers such as those at papermills. Runoff may carry pesticides containing dioxins to water treatment facilities where the organics are incorporated into the sludge, which may then be incinerated. Likewise, contaminated waste materials from some manufacturing processes may be combusted as an energy recovery procedure. Two examples are PCP sludge incinerators used at some wood preserving facilities and black liquor recovery boilers used at paper mills.

Studies of emissions from boilers included in the literature review[3] demonstrate that if PCDD's are detected in the feed of an inefficient or poorly controlled combustion process, it is very likely that they will be emitted to the atmosphere.

3.3.2 Precursors In Feed

Most of the studies reviewed in the literature search[3] focused on the formation of dioxins and furans from precursors. Esposito et al. presented detailed descriptions of these formation mechanisms for chlorinated dioxins.[39] This work organizes dioxin precursors into three classes:

Class I - Polyhalogenated phenols, primarily with a halogen ortho to the hydroxyl group, with a high probability of dioxin formation;

Class II - Ortho-halophenols and ortho-halophenyl esters where the substituted groups are a mixture of halogens and nonhalogens; and

Class III - Other chemicals having the possibility, but less likelihood, of dioxin formation, including chlorinated aromatic compounds.

The majority of experimental work to date has centered on three classes of precursors: chlorinated phenols, chlorinated benzenes, and PCB's. Dioxin formation from the combustion of chlorinated phenols has been tested extensively by Rappe[40] Jansson[41], and Ahling[42,43]. Dechlorination of highly chlorinated homologues can result in formation of the more toxic 2378-TCDD isomer. Chlorinated phenols are used as wood preservatives, herbicides, and for sap stain control. Wood or vegetation sprayed with chlorophenols may be disposed of by incineration or used as a supplemental fuel in boilers. In addition, chlorophenol wastes are often disposed of in sludge incinerators and industrial boilers. The identified references above provide a reasonable basis for considering these combustion sources as likely sources of dioxin emissions and therefore, candidates for the Tier 4 testing program.

Buser investigated the formation of PCDD's and PCDF's from the pyrolysis of chlorobenzenes.[44] The formation mechanism included a chlorophenol and a polychlorinated diphenyl ester (PCDPE) intermediate. Chlorobenzenes are used in solvents, dyes, pharmaceuticals, and rubber production. Such products make up much of the organic chlorine found in municipal waste incinerator feed. The associated waste products may also be disposed of in other incinerators or boilers.

Buser also investigated the formation of PCDF's from the pyrolysis of PCB's.[45-47] No experimental work has been identified on PCDD formation from PCB's. However, several studies have been identified that found PCDD's emitted from PCB fires.[23,37,48] In addition, PCB's are frequently in solution with hexachlorobenzenes which have been shown to form PCDD's. PCB's have been used

as dielectric fluids, in transformers and capacitors hydraulic fluids, plasticizers, and dyes. The incineration of PCB's at waste disposal facilities or in boilers may result in PCDD and PCDF emissions.

3.3.3 Chlorine In Feed

The chlorine content of fuel is obviously an important parameter affecting the formation of PCDD's or PCDF's. Shih et al. developed a ranked priority list of conventional combustion systems emitting polycyclic organic matter including PCDD's and PCDF's.[49] The rationale presented for source ranking is based on fuel characteristics and combustion conditions. Shih's work places great emphasis on both the chlorine content of the feed and the concentration of aromatics in the feed.

Various authors have demonstrated the effect of chlorine on dioxin emissions. Mahle et al. demonstrated that PCDD's were emitted from coal combustion only when chlorine was added.[50] Tiernan et al. found PCDD formation during the combustion of pine in the presence of HCl, but no PCDD's were detected during the combustion of pine alone.[51] Liberti studied the combustion of vegetables.[52] When inorganic chlorine or PVC were added, PCDD's and PCDF's were detected in the feed. While there is general acceptance that some chlorinated compounds are conclusive to dioxin formation, these inorganic chlorine studies demonstrate that the specific mechanisms involved in PCDD formation are complex and not well understood. However, it can be generally stated that chlorine must be present for the formation of PCDD, and general trends suggest that increased chlorine concentrations in the feed may improve the possibilities of PCDD emissions.

3.3.4 Combustion Conditions

The remaining factors that are believed to significantly affect PCDD emissions are combustion conditions. These are combustion temperature,

residence time, mixing, use of supplemental fuel, and fuel processing. The overall combustion efficiency of a combustion process is a function of all of these factors. In order to destroy PCDD's or prevent their formation, the combustion efficiency must be high. This requires a combination of high temperatures, available oxygen, high heat content fuel, and long residence times. Each factor is discussed separately below.

3.3.4.1 Combustion Temperature

Experimental evidence suggests that temperatures of 500-800°C promote PCDD formation, while temperatures greater than about 800°C destroy PCDD's.[1,43,47] Buser et al. showed that PCB pyrolysis at 550-650°C forms PCDF.[47] However, pyrolsis at temperature greater than 700°C cause 99 percent destruction of PCB's and no PCDF formation.[38] Ahling et al. produced similar results for both PCDD's and PCDF's during the combustion of chlorophenols.[42]

Combustion temperature is a function of the BTU (British Thermal Unit) content of the fuel or supplemental fuel, the available air, and the degree of fuel processing. Municipal waste incinerators are considered a significant combustion source of PCDD's.[14-19] These large mass burn units are characterized by low combustion temperatures, due in part, to the high moisture, low BTU content of the fuel; poor air/feed mixing due to the lack of feed processing; and lack of supplemental fuel. In comparison, many hazardous waste incinerators and high efficiency boilers are designed for very efficient combustion. These units burn high BTU fuels and/or add high BTU supplemental fuels; and, even if the air/fuel ratio is low, the air/fuel mixing is efficient. The fuels are processed (e.g., drying, shredding, combustibles separation, etc.) to decrease mositure and improve mixing. In many cases, high temperature afterburners are used for the combustion of offgases. Several studies have identified the effects of high combustion temperatures on PCDD's and PCDD precursors.[22,23,26] For example, no

PCDD's were detected in the emissions of the Vulcanus incinerator ship during the combustion of PCDD contaminated Herbicide Orange.[22] The combustion temperature during this project was 1600°C.

3.3.4.2 Residence Time

The residence time necessary to destroy PCDD's and the combustion temperature are inversely related. The higher the combustion temperature, the shorter the required residence time for PCDD destruction. Likewise, a low temperature will require a long residence time for destruction of PCDD's. Sachdev et al. showed that an increase in both temperature and residence time decreased the formation of PCDD's from chlorophenol combustion.[53] Similar results have been found at hazardous waste incinerators that run with 1.5-2.0 second residence times. Combustion sources with longer residence times and high temperatures are less likely to form products of incomplete combustion, such as dioxins.

3.3.4.3 Oxygen Availability

Oxygen availability is a function of both the air/fuel ratio and air/fuel mixing efficiency, both of which are of concern when burning solid fuels. Solid fuels and high viscosity liquid fuels (waste tars, etc.) burn as particulates or large droplets, and therefore portions of the fuel are burned in low oxygen or pyrolysis conditions. A low air/fuel ratio or poor air/fuel mixing will promote poor combustion conditions and the formation of PCDD's. Jansson demonstrates that an insufficient air supply increases PCDD emissions from chlorophenol combustion.[41] Muncipal waste combustors are usually fired with excess air. However, large mass burn units have poor air/fuel mixing due to the lack of fuel processing. Activated carbon regeneration and wire reclamation incinerators are both designed with limited air (some wire reclamation is done,

in poorly designed nearly open chambers which are conducive to low temperatures and mixing). All of these cases have been shown to emit dioxins.[14,32,35] Sources with a low air/fuel ratio or poor air/fuel mixing will be considered potential sources of PCDD emissions.

3.3.4.4 Feed Processing

The feed material for a combustion source may be a liquid, a solid, or a gas. Both liquid and gaseous fuels can be easily mixed with air resulting in a high combustion efficiency; solid feeds usually require some processing to improve combustion. Often solid feeds require drying, shredding, or separation to improve combustion. Similarly, high viscosity fuels, for example waste tars, require some preparations including preheating and atomization prior to combustion.

Feed processing will determine, in part, both oxygen availability and residence time. Fine, homogeneous feed particles will improve air/fuel mixing and combustion. Larger particles will require longer residence times and may result in local oxygen deficiencies due to poor mixing. High moisture will also decrease combustion efficiency. Therefore, highly processed homogeneous feeds are less likely to emit products of incomplete combustion, such as PCDD's.

3.3.4.5 Supplemental Fuel

When burning a low BTU fuel, the addition of supplemental fuel will increase the combustion temperature and improve combustion. Haile et al. tested a boiler cofiring RDF with coal.[12] The boiler temperature was 1200°C, and no PCDD's were detected. Dow Chemical tested an industrial incinerator burning waste tars without supplemental fuel and found parts per billion (ppb) levels of TCDD's in the fly ash.[5] After the addition of a supplemental fuel, no TCDD's were detected.

When selecting sources for the Tier 4 testing program, sources fired with high BTU supplemental fuel will be considered less likely to emit PCDD's. Sources burning low BTU wastes without supplemental fuels will be given higher priority for testing.

3.4 Identification Of Source Categories With A Potential To Emit Dioxin

The previous paragraphs have identified a number of parameters which are likely to affect the presence and/or magnitude of dioxins emitted from combustion sources. In the analysis described below, various combustion source categories are reviewed to determine which exhibit characteristics more closely associated with these parameters. Source categories so identified are given a higher priority for source sampling under Tier 4.

A broad list of combustion source categories is provided in Table 3-3. These source categories were examined in a somewhat judgmental manner with the combustion related parameters previously described. This process resulted in a listing of combustion source categories (see Table 3-4) which are considered to be more closely associated with these parameters. Table 3-4 also includes those source categories where dioxin has previously been found to be emitted. Source categories in Table 3-4 represent those which are likely candidates for source sampling under Tier 4.

A number of source categories initially listed in Table 3-3 do not appear in Table 3-4. These have been excluded for a variety of reasons. For example, fossil fuel-fired boilers, process heaters, and gas turbines have been excluded because of their use of fuel with relatively low chlorine content. For the same reason, industrial processes using low chlorine fossil fuels, such as the production of carbon black and coal gasification, have not been included.

Other sources have not been included in Table 3-4 because they are relatively small sources burning a low annual tonnage of fuels. Examples included

TABLE 3-3. COMBUSTION SOURCES

Fossil Fuel Boilers, Process Heaters, or Engines	Waste Disposal Operation	Industrial Processes	Accidental Fires
Boilers --- coal-fired --- oil-fired --- natural gas-fired --- liquefied petroleum gas --- wood Process Heaters --- oil --- natural gas --- refinery gas Turbines --- oil --- natural gas Internal Combustion Engines --- stationary --- mobile Home Heating --- oil --- natural gas --- coal --- wood stoves/fireplaces	Industrial Incinerators Bagasse Boilers Wood Waste Burners Refuse Derived Fuel Boilers Municipal Waste Incinerators Hazardous Waste Incinerators --- land based --- incinerator ship Sewage Sludge Incinerators Waste Oil Boilers Cement/Lime Kilns (Waste Fired) Pathological Incinerators Open Burning Agricultural Burning	Catalytic Cracking Charcoal Manufacturing Carbon Black Manufacturing Coke Manufacturing Coal Gasification Asphalt Manufacturing Coffee Roasting Meat Smoke Houses Black Liquor Recovery Boilers (kraft paper mills) Carbon Reactivation	Electrical Transformers Structural Fires Forest Fires Subway Fires

Table 3-4. COMBUSTION SOURCE CATEGORIES BELIEVED TO HAVE THE GREATEST POTENTIAL TO EMIT DIOXINS

Source	Rationale
Hazardous Waste Incinerators	TCDD[1] Detected
Municipal Waste Incinerators	TCDD Detected
RDF[2] Boilers	TCDD Detected
Commercial Waste Oil Boilers	TCDD Detected
Industrial Boilers Co-firing Wastes	TCDD Detected
Wire Reclamation Incinerators	TCDD Detected
Activated Carbon Regeneration	TCDD Detected
PCP[3] Sludge Incinerators	TCDD Detected
Sewage Sludge Incinerators	PCDD[4] Detected
Mobile Sources	TCDD Detected
Wood Stoves/Fireplaces	TCDD Detected
Industrial Incinerators	TCDD Detected from municipal incinerators
Wood/Bark Boilers	Experimental results with PCP treated wood
Charcoal Manufacturing	Experimental results with PCP treated wood, combustion conditions
Black Liquor Boilers	High POM[5] effluent, PCPs in feed
Cement/Lime Kilns Co-firing Wastes	Precursors present
Small Spreader-Stoker Coal Boilers	Favorable combustion conditions for dioxin formation

[1]TCDD refers to the tetra homologues as a group. Available analyses are mixed, with some researches reporting "total tetras" and others reporting 2378-TCDD or both. The presence of TCDD's generally indicates some likelihood of 2378-TCDD being present.
[2]RDF = Refuse Derived Fuel.
[3]PCP = Pentachlorophenol.
[4]PCDD = Total of all dioxin homolgues or Polychlorinated dibenzo dioxins. While dection of PCDD's does not necessarily indicate presence of TCDD or 2378-TCDD, there are sufficient data to infer such in this case.
[5]POM = Polycyclic Organic Matter.

coffee roasting and meat smoke houses. Similarly, intermittent, small sources, such as structural fires have been excluded. While some of these sources may possibly emit 2378-TCDD, these source categories are less likely to pose an exposure problem than larger sources.

3.5 Development Of Criteria For Prioritizing The Candidate Source List

Since it will not be possible due to resource constraints to stack test each of the candidate combustion source categories listed in Table 3-4, a method for prioritizing the candidate source categories was developed. The method is admittedly subjective, since no realistic assignment of weighting factors could be made for the ranking criteria. Criteria and the "decision tree" used to prioritize the candidate source categories are illustrated in Figure 3-1.

Based on these criteria, candidate source categories were placed into one of the four groups listed in Table 3-5. Table 3-5 also presents the grouped source category list. The source categories within a particular group are not listed in any particular order. The Rank A group represents source categories that have not yet been extensively tested and which are expected to be the most likely to emit dioxins. Rank B and C groups also have a fairly high likelihood of emitting dioxins but are hypothesized to emit less than Rank A sources. Rank D source categories have been tested three or more times.*

3.5.1 Rank D Source Categories

Rank D source categories include municipal waste incinerators and industrial boilers co-firing wastes. Six municipal waste incinerators have been

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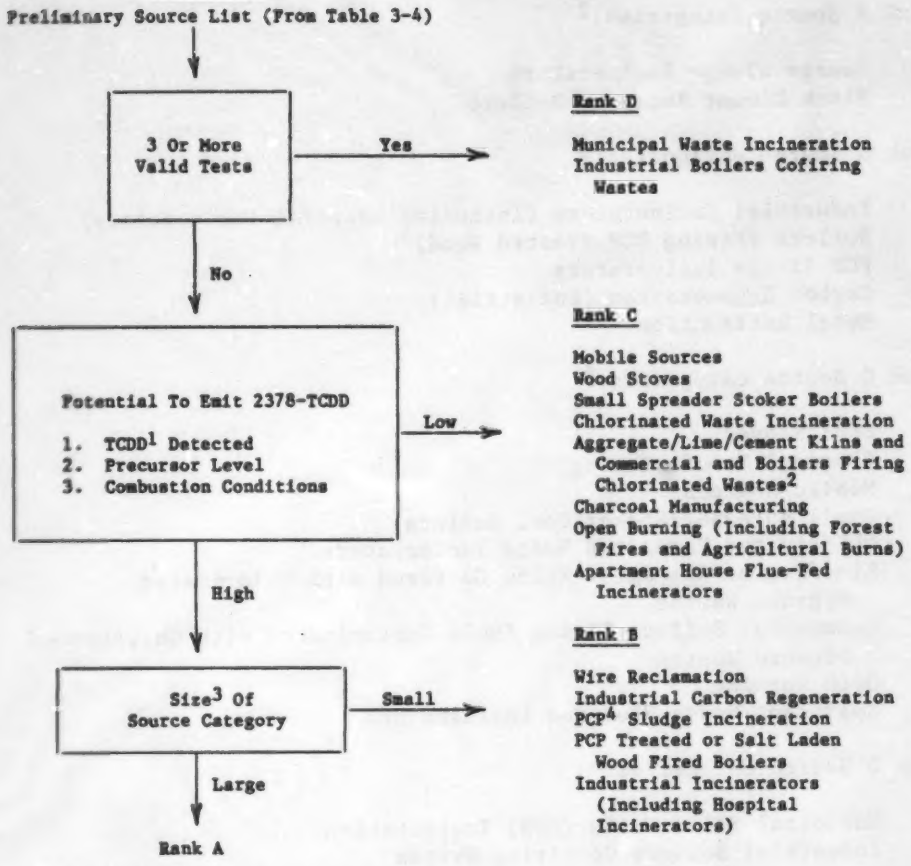
*As described in Appendix A, it is believed that data from three different sources provides a reasonable amount of data to characterize a particular source category for this effort. Appendix A also demonstrates that it will not be possible to obtain statistically significant results under Tier 4, since it is not possible to test enough sources under this program to obtain a rigorously representative sample to be able to develop meaningful confidence limits and account for variabilities that exist among sources.



[1]Some researchers have reported only the total for the tetra homologue. The presence of TCDD is assumed for this ranking procedure to be adequate to indicate the potential to emit 2378-TCDD.

[2]Commercial Boilers firing chlorinated wastes could be a higher ranked category. However, they have been ranked C based on research on Industrial Boilers firing chlorinated wastes and pending regulations to prohibit chlorinated waste disposal in commercial boilers.

[3]"Size" of category takes into consideration the number of sources, their emission volume and general location with respect to exposed populations.

[4]Contacts with sources identified as incinerating PCP sludges in boilers indicate that these sludges are now generally landfilled.

Figure 3-1: Ranking Criteria and Decision Tree

Table 3-5. Ranked Source Category List For Stack Testing[1]

Rank A Source Categories:[2]

Sewage Sludge Incinerators
Black Liquor Recovery Boilers

Rank B Source Categories:[3]

Industrial Incinerators (including hospital incinerators)
Boilers (Firing PCP treated Wood)[4]
PCP Sludge Incinerators
Carbon Regeneration (industrial)
Metal Reclamation

Rank C Source Categories:[5]

Wood Stoves
Charcoal Manufacturing
Mobile Sources
Small Spreader-Stoker Coal Boilers
Chlorinated Hazardous Waste Incinerators
Lime/Cement/Aggregate Kilns Co-fired with Chlorinated Organic Wastes
Commercial Boilers Firing Fuels Contaminated with Chlorinated Organic Wastes
Open Burning
Apartment House Flue Fed Incinerators

Rank D Source Categories:[6]

Municipal Solid Waste (MSW) Incineration
Industrial Boilers Co-firing Wastes

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[1]The list of combustion source categories under investigation by Tier 4 continues to be revised as new information is received and is therefore subject to change.

[2]Rank A are large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination of feed/fuel. These categories are judged to have a high potential to emit TCDD.

[3]Rank B are small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have some potential to emit TCDD.

[4]PCP is an abbreviation for pentachlorophenols.

[5]Rank C are source categories less likely to emit TCDD.

[6]Rank D are source categories which have already been tested three or more times.

tested for dioxin in the United States.[11-15] By December 1985, it is expected that seven additional dioxin tests will have been performed on municipal waste incinerators in industrial boiler tests have been analyzed. Because more than three stack tests the U. S. Several fly ash and stack tests have also been conducted in Canada and Europe.[16-20] Similarly, archived samples from six waste fired, have been conducted for both of these source categories, they were not considered for additional testing under Tier 4.

3.5.2 Rank C Source Categories

Rank C source categories are those which have been judged to be less likely to emit dioxins when compared to the other candidate source categories. This is based on the following factors: (a) the level of tetrachlorinated dioxins detected in previous tests, (b) the anticipated level of precursors in the fuel/feed, and (c) the likelihood of conditions favorable to incomplete combustion. Rank C source categories include mobile sources, wood stoves, wood boilers, small spreader-stoker coal boilers, chlorinated hazardous waste incinerators, lime/cement/aggregate kilns and commercial boilers burning chlorinated wastes, charcoal manufacturing, open burning and apartment house flue-fed incinerators.

Mobile sources have been tested in two earlier studies.[5,34] In both cases, 2378-TCDD was detected at the part per trillion (ppt) level in particulate matter scraped from exhaust systems or in filtered exhaust samples. Chlorine content of the gasoline and diesel fuels are also low (0-100 ppm). Based on those earlier tests and chlorine content, mobile sources have been ranked C.

Wood stoves have been tested by Dow Chemical.[5,33] 2378-TCDD was detected in chimney scrapings up to 100 ppt. The chlorine content of wood is less than 100 ppm. Although the combustion conditions found in wood stoves favor the formation of dioxins, the low chlorine concentrations and the low

levels of dioxins detected in earlier studies indicate that this category may not emit high levels of 2378-TCDD. Nevertheless, 48 million tons of wood are burned annually, so the potential exposure could be considerable. Wood-fired boilers burning untreated wood, which are more efficient combustion systems, are also ranked C.

Small, spreader-stoker coal boilers have also been placed in the Rank C category. This source category was ranked in this manner because of combustion conditions which favor dioxin formation (e.g., relatively low combustion temperatures and poor air/fuel mixing due to large feed size). It should be noted that tests on high temperature, coal-fired utility boilers have not detected dioxins in stack emissions.

Charcoal manufacturing is a source category with combustion conditions which favor dioxin formation. Furnace temperatures are kept low (500°C), and both air/fuel ratio and air/fuel mixing are poor.[54] While source category surveys indicate that some charcoal manufacturers may use scrap wood from saw mills, most use forest scraps. Approximately three to four million tons of wood are used annually in the production of charcoal.[54] The majority of charcoal manufacturing facilities are located in rural settings. For these reasons, this source category was ranked C.

Another Rank C source category is commercial boilers co-firing wastes. Approximately 6 million tons of Resource Conservation and Recovery Act (RCRA) wastes, many of which are chlorinated aromatics, may be disposed of in commmercial boilers annually.[55] However, studies on industrial boilers have detected only low concentrations of dioxins. In addition, combustion of chlorinated wastes in commercial boilers will most likely be prohibited in the future. For these reasons, the category is ranked C.

Both hazardous waste incinerators and kilns co-firing wastes have been ranked C. Elevated levels of chlorinated dioxin precursors can be expected in the feed of these source categories. However, previous tests have shown that relatively low levels of dioxin are emitted.[23-26,36] This is due to combustion conditions which are not favorable to dioxin formation. Combustion temperatures for these sources are usually greater than 1000°C, and the residence time for fuel ranges from one to two seconds. The use of high BTU supplemental fuel and afterburners also decreases the likelihood of dioxin emissions from these sources.

Agricultural burning, forest fires and flue-fed apartment house incinerators are possible dioxin sources recommended for testing by Tier 4. Burning of harvest residues and forest fires where phenoxy herbicides have been applied may be dioxin sources. Since dioxins are emitted from municipal waste combustion, smaller, less efficient apartment house incinerators may also emit dioxins. There are many of these units in urban areas, especially in the Northern U. S., with approximately 2000 in the New York City area alone. The flue-fed incinerators have the greatest potential of poor combustion conditions.

3.5.3 Rank B Source Categories

Sources with high potential to emit are ranked A or B. Rank B source categories are smaller source categories (less than one million tons of fuel burned per year) or are categories with lower concentrations of precursors in the feed. These include PCP sludge incineration, carbon regeneration, industrial incineration, wire reclamation and high chlorine or PCP treated wood fuel boilers.

PCP sludge incineration has been evaluated in two studies.[30,56] In both cases, PCDDs were detected in fly ash samples. Through experimental studies, PCPs have been shown to form octachlorodibenzo-p-dioxins (OCDD) during

combustion.[41] Dechlorination of OCDD can produce lower chlorinated dioxins and thus 2378-TCDD.[29] Annually, 19,000 tons of PCP are used to preserve wood.[57] Only a small percentage of this is incorporated into sludge which must be disposed. Historically, the sludge is incinerated at the wood preserving plant, along with scrap wood. Contacts with facilities thought to incinerate PCP sludges indicate a recent trend towards landfilling of the sludge. Where sludges are incinerated, it is exptected that a lack of feed processing and a high moisture content sludge can result in poor combustion conditions. Therefore, PCP sludge incineration is a potential source of dioxin emissions.

Industrial activated carbon regeneration, where activated carbons is heated to drive off captured organics, was also been ranked B. In order to prevent the combustion of the carbon during the carbon regeneration process, the air/fuel ratio and the combustion temperature (800°C) are kept low.[58] These conditions are conducive to incomplete combustion. The thermal regeneration of activated carbon has been studied at one source, where the spent carbon had been used to treat a water supply system.[32] Ppt levels of TCDDs were detected in the fly ash and stack emissions. Precursor levels in the municipal water treatment carbon are low in comparison to what may be expected in carbon used to treat an industrial waste stream.

Industrial incinerators, including hospital incinerators, are also ranked B. There are approximately 3000 of these units in the United States.[59] These incinerators have many applications including disposal of high organic chlorine wastes such as industrial waste plastics and used medical supplies. One industrial incinerator burning municipal solid waste has been tested and low levels of 2378-TCDD were detected.[14] An industrial incinerator burning a more chlorinated organic waste, such as chlorinated plastics, is a possible dioxin source.

Another Rank B source category is wire reclamation incinerators where plastics are burned off wire and other electrical equipment to reclaim metals, especially copper. In previous tests, ppt levels of TCDDs were detected in ash samples.[35] As with carbon regeneration and charcoal manufacturing, both the combustion temperature and available oxygen are kept low in this process.[60] Wire insulation incinerated during the process often contains PCBs and polyvinyl chloride.

The final Rank B source category is boilers burning salt laden wood or wood that has been treated with PCP. This source category was ranked on the large volume of wood burned in the U. S. and the results of laboratory studies where dioxins were formed in the pyrolysis of wood in the presence of HCL. Burning salt laden wood, that has been stored in salt water, can result in a flyash with a chlorine salt content of 65 percent.[61] Burning PCP treated wood is of similar concern as PCP sludge combustion with wood.

3.5.4 Rank A Source Categories

The remaining source categories were ranked A. These are sewage sludge incinerators and black liquor boilers.

Approximately 1.5 million tons of sewage sludge are incinerated annually.[62] The sludge is most commonly burned in a series of hearths to reduce bulk and recover energy from volatiles in the sludge. Fluid bed combustion is also used. The high moisture content of the feed can result in poor combustion conditions. In addition, sewage from an industrial area may contain elevated levels of PCBs and other chlorinated aromatics. In an earlier Canadian study, PCDDs were detected in stack emissions.[27] Many newer units are operated on a fuel efficient system. In order to save energy, both the combustion temperature and the available oxygen are held low, conditions which increase the potential for dioxin emissions.

The other Rank A category is black liquor recovery boilers. Approximately 13 percent of all fuel used in large industrial boilers is pulping liquor.[63] Some 42 million tons of pulping liquor are recovered by burning in boilers of which black liquor boilers are a subcategory.[64] Sources with greatest probability to emit dioxin are those recovering liquor with a higher chlorine (1-3 percent) than most black liquor boilers (less than 1 percent chlorine in the liquor). In order to prevent smelt oxidation, the temperature is often kept below 800°C in these boilers. In addition, earlier studies have detected POM emissions from these boilers.[65]

3.6 Types Of Samples To Be Collected Under The Stack Testing Program

The stack testing program is designed to obtain a quantitative measure of dioxin and furan emissions discharged to the atmosphere from a given source. Gaseous and particulate matter stack samples will be collected, both before and after existing control devices in most cases. Stack emissions will be sampled using methods similar to those described in the newly developed draft ASME sampling protocol.[6,66] This protocol is based on use of an EPA modified Method 5 train with an XAD-2 sorbent.

A summary of the stack testing requirements contained in the protocol is outlined in Table 3-6. A detailed summary can be found in National Dioxin Study Tier 4 - Combustion Sources: Sampling Procedures, EPA-450/4-84-014c.[66] Three independent sampling runs will be made at each site over a period of about one week. The analyses of stack samples will include the tetra and higher dioxin and furan homologues (i.e., penta, hexa, hepta, and octa), and 2378-TCDD. Samples will be analyzed to ppt level of detection (approximately 40 ppt).

Ash, water, soil, and precombustion air samples will be collected in addition to stack samples. Ash samples will be periodically collected during

Table 3-6. SUMMARY OF TIER 4 STACK SAMPLING PROCEDURES[a]

°Sampling procedures will be based on the draft ASME protocol requirements.

- Three separate test runs.
- Sample quantities will allow for initial analysis archiving.[b]
- Stack tests includes the following samples:
  - -- Stack Emissions
  - -- Air Pollution Control Device Inlet Stream[c]
  - -- Grab Samples of Feed/Fuel
  - -- Bottom Ash Grab Samples
  - -- Ash or Slurry from Control Devices
  - -- Precombustion Air[d]
  - -- Quench Water Effluent
  - -- Soil

°Standard EPA Method 5 train, modified to incorporate a sorbent module containing XAD-2.

°Emissions Characterization:

- Stack Temperature
- Stack Gas Flow
- Moisture Content
- CO_2, CO, O_2, NO_x, THC (continuous monitoring)
- HCl, SO_x Opacity (where appropriate)

[a]Data requirements set forth in the ASME protocol will be collected as appropriate. Since the ASME protocol is directed toward municipal waste incinerator tests, actual data collection for Tier 4 sites may vary. For example, opacity continous instack monitoring data after a wet scrubber may not be very meaningful but an HCl sampling train may provide information on available chloride in flue gases. See Reference 66.

[b]Except most stack samples.

[c]Except uncontrolled sources or where data is not meaningful.

[d]Only at site where dioxin or precursors may be present in intake air.

each of the stack test runs and composited daily. As described later, comparisons of the magnitude of dioxin in the ash with that in the flue gas are planned. Analysis of ash samples may identify potential disposal problems which may exist if high levels of dioxins and furans exist in the ash. Procedures for collection of ash samples are also described in Sampling Procedures[66].

Limited soil samples will be collected at each of the sources, primarily around ash handling areas. Soil samples will be collected using sampling procedures described in Sampling Procedures[66]. Composite soil samples from the various sites will be analyzed for 2378-TCDD, and dioxin and furan homologues.

Precombustion air will be sampled at any source where there are "hits" and any significant dioxin precursors are suspected to be in the air as a result of site contamination. Some heavily industrialized areas for example, could have relatively high (ppb to ppm levels) concentrations of precursors of dioxin in the ambient air. The decision to test precombustion air will be made source-by-source from information obtained during the pretest survey. The criteria for this decision is outlined in the pretest survey protocol described in Section 4. Precombustion air samples will be collected with an ambient sampler described in Tier 4 Sampling Procedures[66]. These samples will be analyzed for 2378-TCDD, and the higher dioxin and furan homologues, PCBs, chlorinated phenols, chlorinated benzenes, and other chlorinated organics.

During the stack test, fuel/feed samples will be periodically collected and composited. The fuel/feed samples will be analyzed for PCBs, total chlorine, chlorinated phenols, and chlorinated benzenes, since these compounds may be precursors of dioxin. If dioxins are detected in the stack emissions, the fuel samples will also be analyzed for 2378-TCDD, and the higher homologues of dioxins and furans. Table 3-7 summarizes the analyses to be performed on each sample collected during the stack test. In addition to the number of samples

TABLE 3-7. SAMPLING AND ANALYSES MODEL

Sample	Method	Samples	Analyses[a]	Total Samples[b] for Analysis	Analysis[c] Priority
Inputs					
Precombustion Air	XAD-2 (Ambient)[d]	0-1[e]	2378-TCDD, 4-8 CDD/CDF[f], TOCL[g], Cl-phenols, Cl-benzenes	1[e]	2
Waste Feed and/or Fuels	Grabs	Daily Composite	2378-TCDD, 4-8 CDD/CDF[f] Cl-phenols, Cl-benzenes, PCB, TOCL[g]	3[f]	2
Outputs					
Stack Before Control	MM5T[h]	Condenser Rinse Adsorbent Resin	2378-TCDD, 4-8 CDD/CDF[f]	3	2
Stack After Control	MM5T[h]	Filter(s) Catch Probe Rinse	2378-TCDD, 4-8 CDD/CDF[f]	3	1
Bottom Ash	Grabs	Daily Composite	2378-TCDD, 4-8 CDD/CDF[f]	3	1
Ash From Control Device	Grabs	Daily Composite	2378-TCDD, 4-8 CDD/CDF[f]	3	1
Other					
Soils (in vicinity)	Borings	1 Composite	2378-TCDD, 4-8 CDD/CDF[f]	1	3
Sampling Train Blanks	MM5T[h]	Resin, Filter(s), Rinses	2378-TCDD, 4-8 CDD/CDF[f]	2	1/2[i]
			TOTAL	19[j]	

[a]Precursor analysis by contractor and dioxin/furan analyses by Troika.
[b]Based on 3 sampling days. Numbers shown are for dioxin/furan samples only.
[c]Priority 1 indicates analyses should be performed for 2378-TCDD and higher (tetra-octa) homologues of dioxins and furans. If there is a detectable concentration, Priority 2 samples are to be analyzed. Priority 3 samples may be analyzed on a case-by-case basis if Priority 2 samples have a positive response.
[d]XAD-2 (ambient) denotes a modified high volume air sampler for ambient organic compounds.
[e]Sample to be collected if there is a significant source of suspected precursors in vicinity of sampling site.
[f]4-8 CDD/CDF = Analyses done on higher (tetra through octa) chlorine number dioxins and furans with results reported as totals for each group only.
[g]TOCL = Total organic chlorine.
[h]MM5T is a modified EPA "Method 5" train as defined in the ASME protocol.
[i]For blank sampling trains, one is designated priority one and the second will be analyzed only if the first blank train has detectable background levels of dioxin/furans.
[j]Multiple analyses for each sample will have a multiplier effect on the analytical costs also. Total does not include quality assurance samples (approx. 20%).

listed in the table, additional analyses will be required for quality assurance/ quality control purposes (blanks, duplicates, blinds etc.).

3.7 Stack Sampling Analysis Priority

Tier 4 has been allocated approximately 700 of the 3600 analyses by Troika for the National Dioxin Study. Estimates of Tier 4 analyses for 10-12 stack and 45-60 ash sampling sites indicate that up to 900 analyses would be required. In order to meet the analyses allocation and to utilize expensive Troika analyses most efficiently, an analyses decision tree was developed. A decision tree reduces the number of analyses performed on samples collected in the field, thereby reducing analytical costs. The guiding principle of the decision tree is to analyze sufficient samples to determine whether or not dioxin enters the environment. Internal process streams would be analyzed only in the event of detection of dioxin in the effluent streams. By using the decision tree, total analytical resource constraints can be met without affecting the Tier 4 goal to assess the risk of dioxin emissions from combustion.

The decision tree will be used to divide field samples into three priorities. Each sample will be identified by the sampling organization prior to submission to the analytical organization on the following priority basis.

Priority 1:

All Priority 1 samples will be analyzed. These samples are identified, such that if the results are negative, a very high probability will exist that Priority 2 and 3 samples will also be negative.

Priority 2:

If 2378-TCDD is detected above the selected criteria value for Priority 1 samples, Priority 2 samples will be analyzed.

Because no minimum level of concern can be initially designated for 2378-TCDD, any 2378-TCDD detected above the determined analytical minimum detection limit will be the criteria for analyzing Priority 2 samples unless higher thresholds are designated by risk assessments.

Priority 3:

These samples will be collected in the field but are not planned for analysis unless a "major" dioxin emission is determined. Therefore, they will be archived by the sampling organization. Analysis of these samples may occur on a case-by-case basis.

To minimize possible sample interferences, aqueous phase samples should be extracted within approximately fourteen days of collection. All aqueous phase samples that require extraction will be identified before submission to Troika.

3.8 Ash Screening Program

The Tier 4 plan includes a program to collect ash screening samples from a number of combustion source categories. The ash sampling program is relatively inexpensive and will provide dioxin related information for several combustion sources. Table 3-8 lists the ranked source categories which have been recommended for ash screening. Additional source categories that have a reasonable liklihood of emitting dioxins may be added to the screening list, based upon recommendations from the EPA Regional Offices and others.

Unfortunately, at this time, collection and analysis of ash samples is not a demonstrated, reliable screening technique to provide conclusive estimates of dioxin emissions from combustion sources. A considerable fraction of dioxins are hypothesized to be emitted as a gas or absorbed upon the fine particulate. If this is true, it would generally not be concentrated in bottom ash or the flyash collected in an air pollution control device. Data are available which

TABLE 3-8. COMBUSTION SOURCE CATEGORIES WHERE ASH SAMPLES WILL BE COLLECTED

Source Categories[1]
Sewage Sludge Incinerators
Black Liquor Recovery Boilers
Industrial Incinerators (Including Hospital Incinerators)
Metals Reclamation (Including Wire Incinerators and Secondary Copper Smelters)
Chemical Sludge Incinerators
Industrial Carbon Regeneration Units
Charcoal Manufacturing Ovens
Wood Stoves
PCP Treated And Salt Laden Wood Combustion In Boilers
Small Spreader-Stoker Coal Fired Boilers
Lime/Cement/Aggregate Kiln And Commercial Boilers Burning
Open Burining (Including Forest Fires And Agricultural Burning)
Apartment House Flue Fed Incinerators

[1]Includes some sources which have been identified by State, Regional, and other EPA Program Offices with reasonable likelihood of emitting 2378-TCDD.

The list of Tier 4 categories continues to be revised as new information is received and is therefore subject to change.

indicate there is likely to be selective partitioning of homologues between those in the flue gas and those in the fly ash.[29] These data imply that, tetra chlorinated dioxins concentrate in the flue gas, while the higher dioxin homologues concentrate in the flyash. As a result, ash samples can only provide a general indication of the presence of dioxin at a source. For example, if 2378-TCDD is found in the ash, it can only be assumed that 2378-TCDD was probably emitted in the flue gas. When 2378-TCDD is not found in the ash, it cannot be assumed that 2378-TCDD is not present in the flue gas. At least at one source, where both stack and ash data were collected from the same source, tetra chlorinated dioxins were found in the flue gas, even though no tetra-octa chlorinated dioxins were found in the fly ash.[17] Ash samples can probably now best be used as a screening tool to identify those source categories which have a likelihood of emitting dioxin and which probably should be stack tested.

Despite the limitations associated with these samples, ash sampling is expected to be useful. Ash sample data collected by Tier 4 may provide additional data to qualitatively indicate if dioxin and furan are emitted from source categories not stack tested. Results of stack and ash programs will be augmented by other studies outside of Tier 4 in the development of any hypotheses on the scope and magnitude of dioxin emissions from combustion sources as well as the combustion conditions which are conducive to such emissions.

Section 4

Implementation Of The Tier 4 Plan

4.1 Overview

The previous section identified the specific source categories to be sampled under Tier 4. This section focuses on how individual sources are being selected for testing and who is responsible for various activities under Tier 4. This section also discusses the management and coordination aspects of Tier 4.

4.2 Selection Of Individual Sources For Testing

Ash and/or stack samples will be collected from approximately three sources within each of the source categories which has been selected for testing. The process of selecting individual sources for testing within each of the source categories will be coordinated with the EPA Regional Offices. The EPA Regional staff have been asked to recommend certain sources from amongst these sources meeting model criteria for ash screening or stack testing. In selecting these sites, the Regions and Tier 4 management must consider a number of practical constraints.

For example, accessibility to a site will be an important factor. While Section 114 authority of the Clean Air Act will be used to gain access to particular facilities, if necessary, it is more practical to select sites where accessibility is not a problem. The support and cooperation of State/local agencies is also being incorporated into the study since much of the ash sampling program will be conducted with EPA Regional Offices for sources located within their jurisdiction. Selecting sites in those States which provide assistance and cooperation facilitates sample collection.

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4.3 Ash Sampling Program

As individual sites are approved for the ash sampling, the appropriate Regional and/or State Office(s) are contacted to arrange for the collection of the ash samples. Arrangements include obtaining access to the site and providing specifics of the facility ash handling system and other information regarding the site(s) to Tier 4 ash program management. This information determines what sampling kits and guidance will be sent to the Regional and/or State Office to collect the samples.

Specific guidance on the types of information to be collected and how the ash samples are to be collected has been developed. The ash sampling plans and procedures are described in two Tier 4 documents: Sampling Procedures, EPA-450/4-84-014c[66] and Ash Sampling Program, EPA-450/4-84-014d.[67] Ash samples are to be collected from particulate matter control devices, or from the ash pit, in the event no control device is used. Samples from open burning will be collected from ground surfaces and will not include soil substrate. Multiple samples collected at a site will be combined into a single composite for each site. A portion of this composite sample will be stored for possible follow-up analyses.

Equipment and detailed procedures needed to collect, package and ship samples to the Troika for analysis are provided in the Ash Sample Program document.[67] Briefly, each sample is assigned an episode number by the Sample Control Center which has been established to manage the influx of samples to the Troika under the National Dioxin Study. Episode numbers are provided to Tier 4 management which assigns sample numbers. Episode and sample numbers are then forwarded to the sampling group (Region or State). Once samples are analyzed, the results will be validated by the laboratory before being released to Tier 4. Tier 4 will authorize the validated data to be made available to the Regional Offices.

4.4 Stack Testing Program

Similar procedures are used to identify individual sources for the detailed stack testing program. Tier 4 has identified general source characteristics believed to be representative of the source categories to be stacked tested. This information has been sent to the EPA Regions, who have recommended some sources for testing. The Tier 4 sampling contractor selects possible sampling sites from these recommendations as well as sites identified from industry contacts and EPA reports. Once selected, the contractor initiates the process of gaining access in coordination with the Regional/State/local agencies. After access to a possible testing site has been agreed upon, the Tier 4 contractor and, for some sites, an EPA representative visit the source to make a pretest survey to obtain the necessary information needed to make a final testing decision and plan the source test. When a site is finally selected, a site specific test plan is prepared by the contractor and submitted to Tier 4, the Region, and a quality assurance contractor prior to the actual testing. This plan will include:

(a) reference to descriptions of the sampling procedures equipment to be used;

(b) the number of individual source tests to be performed;

(c) the number and types of samples (e.g., before or after controls, feed/fuel, ash, soil) which will be collected;

(d) the location at the source where each sample will be collected;

(e) information on the various operating parameters which will be recorded during source testing; and

(f) procedures to be followed concerning the labeling, storage and shipment of the samples to the Troika for dioxin and furan analysis and to the contractors' laboratory for precursor analyses.

Once the plan is approved, the contractor will make arrangements to proceed with the stack test. EPA personnel will oversee most of the stack sampling, which includes three separate test runs over 5-7 days.

In addition, an independent quality assurance contractor will conduct on site performance and systems audits. These types of audits will be conducted on 20 percent to 30 percent of the stack tests and will evaluate the sampling contractors adherence to the Sampling Procedures document[66] and the Quality Assurance Project Plan, EPA-450/4-84-014e.[68] From these quality assurance audits will come an independent evaluation of the stack sampling program.

After the stack test has been completed, a report will be prepared for each source tested. A guidance manual, has been prepared for dioxin and furan source test reports for testing data to be used in Tier 4. The guidance document will assure consistency and comparability for Tier 4 data. The report is entitled National Dioxin Study Tier 4 - Combustion Sources: Dioxin Source Test Reporting Format Guide, EPA-450/9-84-014f.[69]

4.5 Quantitative Exposure And Risk Assessment

In the event that 2378-TCDD, and higher dioxin and furan homologues are detected in the stack emissions at any of the sources tested, a quantitative exposure and risk assessment for atmospheric concentrations will be performed for that site. Evaluation of inferrences that can be made to other sources within this source category will also be performed. A revised exposure and risk methodology is currently under development by EPA. The Strategies and Air Standards Division (SASD), OAQPS will perform exposure and risk analyses for Tier 4 stack testing results.

4.6 Management Of Tier 4

The responsibility for managing Tier 4 has been assigned to the Office of Air and Radiation (OAR). Within OAR, the Tier 4 program manager is Edward J. Lillis, Chief, Air Management Technology Branch (AMTB). AMTB is part of OAR's Office of Air Quality Planning and Standards (OAQPS), Monitoring and Data Analysis Division (MDAD), Research Triangle Park, North Carolina. The Tier 4 program staff consists of James H. Southerland, William H. Lamason, William B. Kuykendal and Edward J. Hanks within the Air Management Technology Branch.

Technical support for stack sampling methods and test program implementation is being provided to Tier 4 from the Office of Research and Development (ORD), by Donald Oberacker of the Hazardous Wastes Engineering Research Laboratory (HWERL) and Larry Johnson of the Air and Energy Engineering Research Laboratory (AEERL). Tier 4 risk assessments are performed by David Cleverly and Mike Dusetzina of the Strategies and Air Standards Division, OAQPS.

An advisory Tier 4 Work Group, comprised of representatives of various EPA program offices (Table 4-1), has been formed to:

(a) assist OAR in the design and implementation of Tier 4;

(b) seek technical expertise and guidance from other EPA representatives on issues which arise during the project;

(c) provide suggestions on how to accomplish the study objectives;

(d) review and comment on the adequacy of protocols, sampling strategies, source test reports, and other material which may be prepared; and

(e) keep other EPA officials appraised of the status of the project.

4.8 Coordination With The EPA Regional Offices

EPA's Regional Offices are expected to play a key role in the implementation of the Tier 4 program. Regional contacts have been identified in each of the

TABLE 4-1. TIER 4 WORK GROUP

Name	Organization	Mail Code	Telephone Number
Don Barnes	Chlorinated Dioxin Work Group, Washington, DC	TS-788	(202) 382-2897
David Cleverly	Office of Air Quality Planning and Standards, Strategies and Air Standards Division (OAQPS/SASD), RTP, NC	MD-12	(FTS) 629-5645 (919) 541-5645
Jim Cummings	Dioxin Management Coordination Staff, Washington, DC	WH-562B	(202) 382-4686
Mike Dellarco	Office of Research Development (ORD), Washington, DC	RD-675	(202) 382-5794
Paul des Rosiers	Office of Research Development (ORD), Washington, DC	RD-681	(202) 382-2722
Norbert Jaworski	Environmental Research Laboratory, ORD, Duluth, MN	-	(FTS) 783-9550 (218) 727-6692
Larry Johnson	Air and Energy Engineering Research Laboratory (AEERL), RTP, NC	MD-62	(FTS) 629-7943 (919) 541-7943
Steven Kroner	Office of Water Regulations and Standards, Office of Water (OWRS/OW), Washington, DC	WH-553	(202) 382-7027
William H. Lamason	Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division (OAQPS/MDAD), RTP, NC	MD-14	(FTS) 629-5575 (919) 541-5575
Edward J. Lillis	Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division (OAQPS/MDAD), RTP, NC	MD-14	(FTS) 629-5586 (919) 541-5586
Israel Milner	Air Programs Branch, Region III, Philadelphia, PA	3AM12	(215) 597-9000
Donald Oberacker	Hazardous Waste Engineering Research Laboratory (HWERL), Cincinnati, OH	MS179	(513) 684-7696
Garrett Smith	Solid Waste Branch, Region II, New Yorkk, NY	2AWM-SW	(212) 264-3407
James H. Southerland	Office of Air Quality Planning and Standards Monitoring and Data Analysis Division (OAQPS/MDAD), RTP, NC	MD-14	(FTS) 629-5575 (919) 541-5575
Dave Sussman	Office of Solid Waste, Office of Solid Waste and and Emergency Response (OSW/OSWER), Washington, DC	WH-565A	(202) 382-7927
Boniface Thayil	Air and Radiation Branch, Region V, Chicago, IL	5AR26	(312) 886-6054

Region, to establish and maintain lines of communication. A current list of Regional Office contacts is provided in Table 4-2. Briefly, their role is to:

(a) coordinate with Tier 4 on Regional and State plans for dioxin sampling of combustion sources;

(b) recommend combustion source categories for dioxin sampling;

(c) identify potential sampling sites for combustion source categories;

(d) assist Tier 4 in obtaining access to sites selected for ash and stack sampling;

(e) collection of ash samples at screening sites, either directly or by State and local programs;

(f) appraise other Regional Office staff on the scope, objectives and status of Tier 4; and

(g) coordinate with other Regional Office dioxin staff and the designated public affairs liason on community relations issues of Tier 4.

4.9 Additional Information

For additional information on Tier 4, please contact James Southerland or William Lamason at (919) 541-5575 or FTS 629-5575.

Table 4-2

Regional Office Contacts - Tier 4

Region	Name	Organization	Telephone Number
I	Margaret McDonough	Air Programs Branch (RM 2313) U.S. EPA, John F. Kennedy Bldg. Boston, MA 02203	(617) 223-4870 (FTS) 223-4870
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III	Israel Milner	Air Branch (3AM12) U.S. EPA, 841 Chestnut Street Philadelphia, PA 19107	(215) 597-9090 (FTS) 597-9090
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Appendix A

Number Of Sources To Be Tested In A Source Category

The number of individual sources to be tested within each source category depends upon several factors, including the purpose of the testing, the number of sources in the source category which have been tested previously, and the available resources. Calculations have been made to estimate the number of sources within a particular category which should be tested in order to characterize statistically the emissions from the source category.

In order to determine the number of tests needed, information concerning the variability of emissions from the source categories is needed. Since emission data are not available for many source categories, the municipal waste incinerator source category was chosen as an example in Figure A-1 to estimate the number of sources within this category which should be tested. Based on these data, it has been determined that to characterize this source category in a statistically significant manner (i.e., at a 95 percent confidence), between 14-39 tests would be required (see attached). More specifically, 39 tests would be required if the results of each of the six previous tests are used in the analysis. Fourteen tests would be required if certain source tests believed to be nonrepresentative are not considered in the analysis. Assuming a cost of $90,000 per source test (including non-dioxin analyses), it is clear that the entire Tier 4 budget could be spent testing emissions from only one source category for statistically representative results.

While it will not be possible under Tier 4 to sample enough sources to obtain rigorous and statistically significant results, a reasonable number of stack test and ash samplings should be performed in each source category. The

confidence intervals around these mean emissions should be fairly narrow to allow comparison among source categories. The confidence interval around a mean is given by:

$$\bar{X} \pm \frac{t\ S}{\sqrt{n}}$$

The size of the confidence interval, therefore, varies with the size of the sample (n) and the value of the t statistic. The size of the t value varies with the degrees of freedom (number of samples minus one) and the confidence level chosen. Some example values of the t statistic are shown below.

	t Statistic		
Number of Samples	95% C.I.	90% C.I.	$t_{.05}/\sqrt{n}$
2	12.706	6.314	8.99
3	4.303	2.920	2.48
4	3.182	2.353	1.59
5	2.776	2.132	1.24

Inspe tion of the above shows that, beyond three samples, there are diminishing returns. Similarly, the effects of 1/n diminish beyond n=3. For this reason, and for practical considerations (i.e., resources), a sample size of three tests will be considered optimal for the purposes of this study. This approach applies to the number of sources where ash samples or stack samples would be collected.

Figure A-1. Determination of Sample Size For Municipal Waste Incinerators

PROBLEM: Determine number of municipal waste combustors that should be tested in order to estimate the average dioxin emission rate within a 5 ng/m^3 interval with 95 percent confidence.

Municipal Waste Combustors: Total population = 40

Site	TCDD (ng/m^3)
A	240
B	29.7
C	6.3
D	3.15
E	1.2
F	ND

Assume: Sampling from a finite population without replacement

$$n = \frac{N\ z^2\ SD^2}{d^2\ (N-1) + Z^2\ SD^2}$$

n = sample size
N = population size = 40
Z = reliability coeff = 2 (95% confidence)
SD = standard deviation
d = confidence interval = 5 ng/m^3

Case I: (all sites listed)

$\bar{x}$ = 46.7
SD = 87.0

$$n = \frac{40\ (2)^2\ (87)^2}{5^2\ (40-1) + (87)^2} = 39$$

Case II: (drop sites with highest and lowest average TCDD levels)

$\bar{x}$ = 10.1
SD = 11.46

$$n = \frac{40\ (2)^2\ (11.46)^2}{5^2\ (40-1) + 2^2\ (11.46)^2} = 14$$

SOLUTION: In order to estimate average dioxin emission rate for municipal waste combustions, 14-39 sources should be tested. Based on 95% confidence, results would be within 5 ng/m^3 of true mean.